SOLID STATE DIFFUSION OF NITROGEN AND CARBON IN THE Fe-C SYSTEM

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Abstract

The plasma nitriding is a process of thermo-chemical treatment using direct-current glow discharge to improve elemental content of nitrogen to the surface of steel for subsequent diffusion into the bulk of material. An ambient atmosphere was consisted of mixture of nitrogen and hydrogen; temperature should be between 480 and 560 °C. During the plasma nitriding process nitrogen diffuses to the bulk of material and creates nitrides of iron and alloy elements [1]. Properties of plasma nitriding layers are dependent not only on parameters of nitriding, such as duration, temperature, pressure, voltage and nitrogen potential, but it is also dependent on nitride-formed elements [2]. The temperature of ambient atmosphere and the duration of process have significant influence on the depth of nitrided layer (Nht thickness) [3]. Plasma nitriding process is suitable to use for surfacing of deep cavities with small diameter. This article deals with chemical composition and mechanical properties of plasma nitrided layers after chemical-heat treatment process in variously defined depths from surface to core of material. Also the redistribution of alloy elements in depth of nitrided layers was analysed on two different samples which were plasma nitrided by different duration and finally compared. The nitrided layers were applied to samples of DIN 1.7765 steel which were subsequently evaluated by metallographic, OES and microhardness methods. The results of measurement showed connection of chemical composition of alloying elements after chemical-heat treated process with hardness and microhardness. Analyse of nitrided layers in depth were performed in depths to 102 µm.

Keywords: Diffusion; chemical composition, alloying elements; nitride layer

1. INTRODUCTION

The plasma nitriding is usually applied to already heat-treated material, i.e. after heat-treatment process [1]. The aim is to achieve an enhanced surface hardness, better wear resistance, reduced friction coefficient, increase fatigue limit or corrosion resistance. The nitriding process developed nitrides of iron in the diffusion layer which caused low increase of microhardness. The main elements that caused increasing of properties are alloying elements as molybdenum, vanadium, aluminum or chrome. During plasma nitriding process, two layers can be created. On the surface of material established the compound layer consisted of ε-Fe2-3N and γ-Fe_4N phase [2]. The proportion of individual phases is dependent on carbon concentration in steel [1]. This type of layer has been very hard and brittle with good friction and anticorrosion properties [2]. This layer can be very good evaluated by metallographic methods. Many experiments showed that GDOES evaluation of thickness of compound zone is not expedient. The thickness and hardness of γ´-Fe_4N (diffusion layer) depends on quantity and quality of alloying elements [3]. The composition of diffusion layers can be effectively influenced by chemical composition of nitriding atmosphere [3]. The plasma nitriding is usually applied to already heat-treated material, i.e. after heat-treatment process.

This article describes the chemical and mechanical properties of nitrided layers which were created on surface of DIN 1.7765 steel. Steel is very often used in weapon industry for barrels. The depth of diffusion layer of sample was compared with content of alloying elements and interstitial elements such as carbon and nitrogen in depth of layers [2, 3]. This study deals with chemical and mechanical properties of nitriding layers which were created by pressure of 400 Pa. For diffusivity assessment the parameter time were changed from 4 to 8 h. The microstructures of cross-sectional structures were evaluated by 3D opto-digital microscope Olympus DSX 500 and are given in **Figure 1**. The DSX 500 is a high-resolution upright motorized microscope with 13x

zoom optics. The chemical composition of steels was verified for selected chemical elements by Bulk method on BRUKER Q4 TASMAN spectrometer. Thickness and microhardness of plasma nitrided layers were measured by microhardness method in accordance with DIN 50190 standard on automatic microhardness tester LECO LM 247 AT [4]. The thickness of compound layer were measured by 3D optical microscope OLYMPUS DSX 500 equipped by image analysis stream. Experiments are focused on study of diffusivity of plasma nitride layer, especially the influence of time of process increasing and its influence on the redistribution of elements in layers. The mechanical properties of layers and their relation with chemical composition in depth from 0 to 102 µm from the surface of material were studied.

2. MATERIAL AND METHOD

Samples of DIN 1.7765 steel were heat-treated in accordance with **Table 1**. The results showed that the initial structure feature of steel was assessed as homogeneous which corresponded to a low-carbon tempered martensite (**Figure 1**). Both samples were plasma nitrided at the same conditions (time changing) and the parameters of plasma nitriding process are given in **Table 3**. Plasma nitriding process do not caused the change in structures after 4 and 8 h of process.

Table 1 Temperatures of heat-treated steels

Procedure	Temperature (°C)
Salt quenching	940
Salt tempering	650

The chemical composition of steel was verified by an advanced CCD based optical emission spectrometer Bruker Q4 TASMAN (see **Table 2**).

Figure 1 NITAL etched cross-sectional structure of heat-treated sample after plasma nitriding process; 4 hours

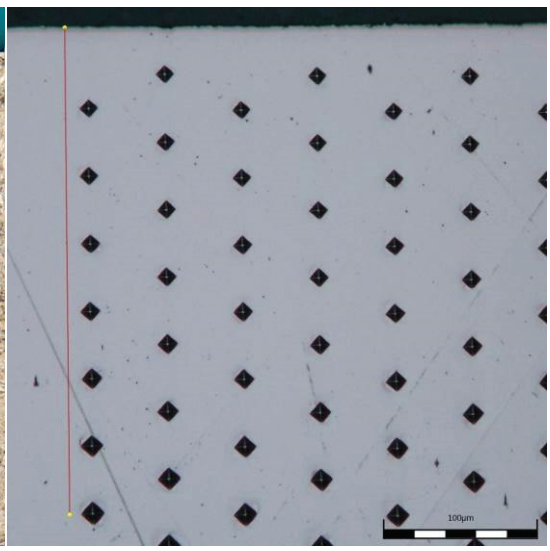

Figure 2 Indentation pattern of microhardness measurement

A microhardness of heat-treated steel of samples was 600 HV 0.05. Plasma nitriding was carried out in PN 60/60 RÜBIG furnace according to **Table 3**. The charge was consisted of 2 samples which were plasma nitrided at the pressure of 400 Pa for 4 and 8 h.

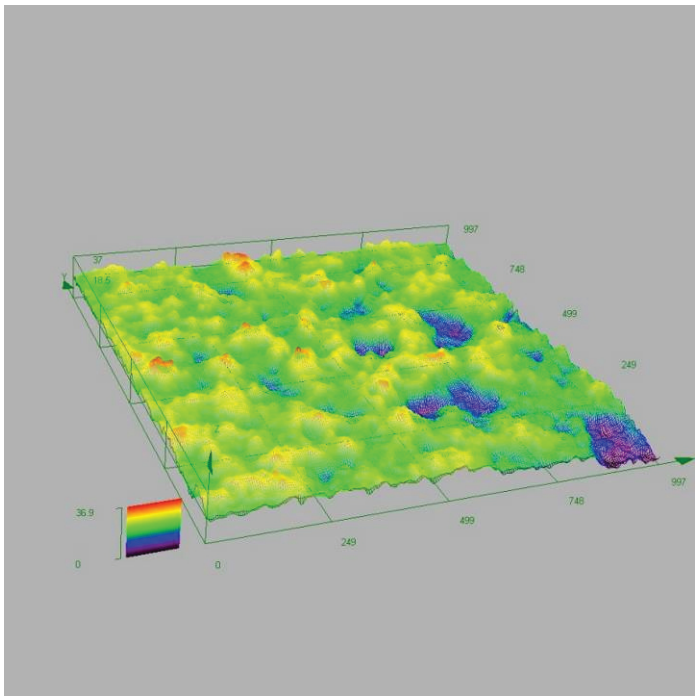

Figure 3 Measured trace (TASMAN Q4)

After plasma nitriding process, the samples were wet grounded using silicon carbide paper with grit from 80 down to 1000 and subsequently polished. Created nitrided layers are documented in **Figure 1**. The chemical composition in depth from 0 to 102 µm was evaluated by Bulk method and results with standard deviations in defined depths are shown in **Table 4**.

Optical spectroscopy measurements were performed in Bruker Q4 Tasman with argon working atmosphere using generator PWM working on Frequency from 50 to 1000 Hz and Spark & arc-like discharges from 10 µs to 2 ms.

Optical 3D optodigital microscope DSX 500 with outstanding resolution of 0.01 µm and magnification range from 17x to 7211x was used for structure documentation. The structure of plasma nitrided sample included compound layer in the top is displayed in **Figure 1** The trace and depth profile after chemical analysing is given in **Figure 3, 4**.

Microhardness was measured by Vickers microhardness method on automatic microhardness tester LM 247 AT LECO at 0.05 kgf load and 10 s dwell time (**Figure 2**). The major Vickers microhardness numbers were derived from five measurements such an average value. The results of five measurements and the cross-section structure of chemical etched material are shown in **Figure 1**.

Table 2 Chemical composition of 1.7765 steel

C	Mn	Si	Cr	Mo	V	P	S
			OES/Bulk Tasman				
0.30	0.47	0.25	2.95	0.89	0.28	0.002	0.001
			DIN standard				
0.30	<	<	2.80	0.80	0.25	<	<
0.35	0.60	0.35	3.20	1.20	0.35	0.025	0.010

Table 3 Parameters of plasma nitriding process

Temperature (°C)	500
Duration (h)	4; 8
Gas flow H_2 / N_2 (l.min^{-1})	24 / 8
Bias (V)	530
Pressure (Pa)	400
Pulse length (µs)	100

Following equation was used for calculation of Nht thickness X (1) in accordance with DIN 50190 standard [4]:

$$X = [(Y * 0.1) * 10] + 50 \quad (1)$$

where, X is Nht thickness in mm, Y is the average microhardness number from five indentations patterns in HV 0.05 [kgf].

Results of alloy elements concentration in mentioned grinded planes from 0 to 102 µm are given in **Table 4** and graphically in **Figure 4**. The analysed profiles after chemical analysing were subsequently replaced by mathematical functions. The grinded planes were verified by using Talysurf CLI 3D Surface profiling as well. The position of centre of gravity was analysed in each of evaporated trace (2).

$$y_t = \frac{\int\int y*dx*dy}{\int\int dx*dy} \quad (2)$$

where $\int\int y * dx * dy$ is static torgue (mm³); $\int\int dx * dy$ is paraboloid area (mm²).

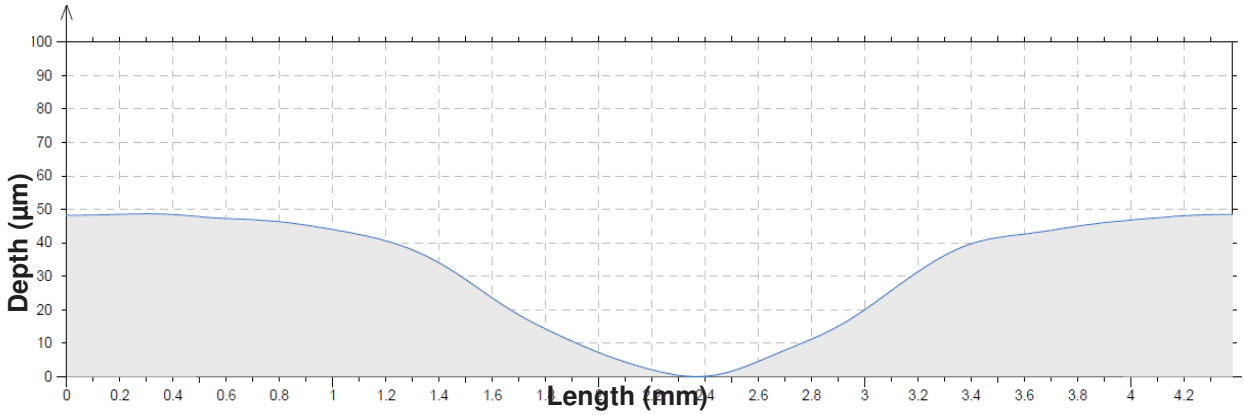

Figure 4 Parameters of profile (2D trace)

Table 4 Mechanical properties and redistribution of alloying elements in layers

Depth (µm)	HV 0.05	Chemical composition (wt. %) Standard deviation							Centre of gravity (CG) (2)
		C	Mn	Cr	Mo	Ni	N	V	
Sample 1 - 8 h									
0	1130	0.207	0.460	2.753	0.835	0.241	2.714	0.250	12
		0.005	0.003	0.016	0.006	0.001	0.132	0.003	
30	1110	0.274	0.445	2.776	0.837	0.228	1.356	0.250	42
		0.003	0.004	0.050	0.014	0.001	0.099	0.001	
60	1030	0.283	0.442	2.781	0.836	0.225	0.613	0.25	72
		0.012	0.362	0.863	0.012	0.001	0.037	0.003	
90	707	0.284	0.446	2.771	0.834	0.225	0.173	0.250	102
		0.008	0.006	0.010	0.005	0.005	0.060	0.002	
Sample 2 - 4h									
0	932	0.232	0.451	2.744	0.847	0.224	1.736	0.254	12
		0.001	0.002	0.010	0.003	0.003	0.050	0.002	
30	716	0.173	0.452	2.737	0.843	0.229	1.743	0.254	42
		0.011	0.007	0.013	0.013	0.006	0.014	0.004	
60	597	0.250	0.448	2.761	0.840	0.224	1.593	0.248	72
		0.017	0.002	0.014	0.010	0.002	0.017	0.001	
90	540	0.271	0.447	2.770	0.841	0.223	1.496	0.248	102
		0.004	0.004	0.003	0.003	0.003	0.068	0.002	

3. RESULTS AND DISCUSSION

The values of chemical composition in grinded planes were subsequently evaluated. The results after 4 h plasma nitriding process are displayed in **Figure 4**. The value of surface microhardness was increased from 500 HV 0.05 to 932 HV 0.05 in case of 4 h plasma nitriding process (compare **Table 4**). Duration of plasma nitriding process caused the other increasing of surface hardness from 932 HV 0.05 to 1130 HV 0.05 (**Table 4, Figure 5**). The development in carbon concentration is more significantly that in the case of 4 h process. The microhardness trends are getting down with increasing depth what is documented in **Figure 4**. The slope of tangent of nitrogen concentration after 4 h has significantly different slope than in case 8 h process. The increasing of duration of plasma nitriding process brings the increasing of surface hardness just to the depth 40 µm in case of steel 1.7765. Continuance on temperature causes nitrogen redistribution and decreasing of nitrogen level and microhardness in layer what is represent in **Figures 4, 5**.

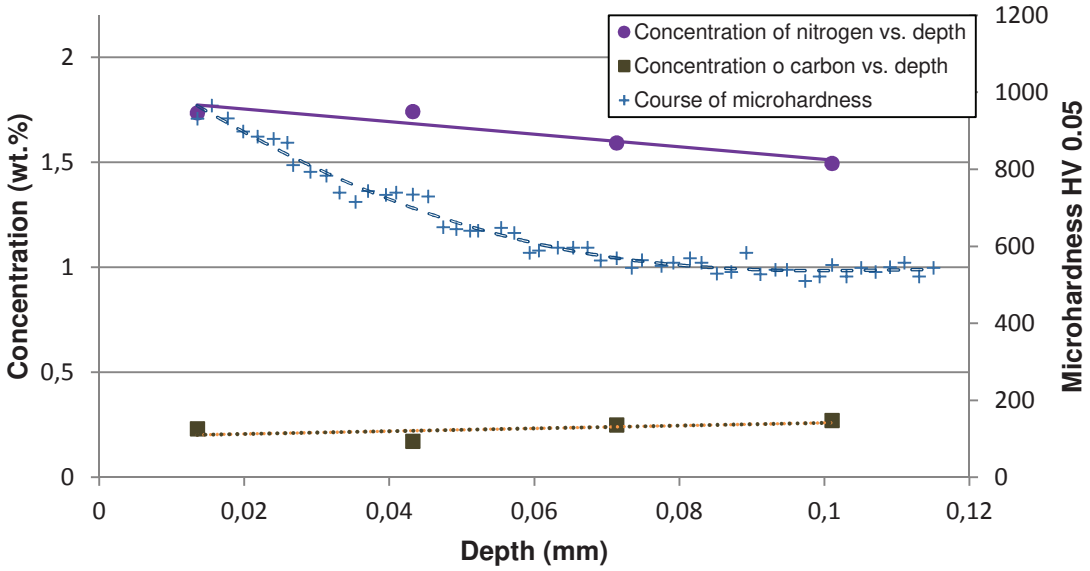

Figure 4 Redistribution of elements after 4 h plasma nitriding process

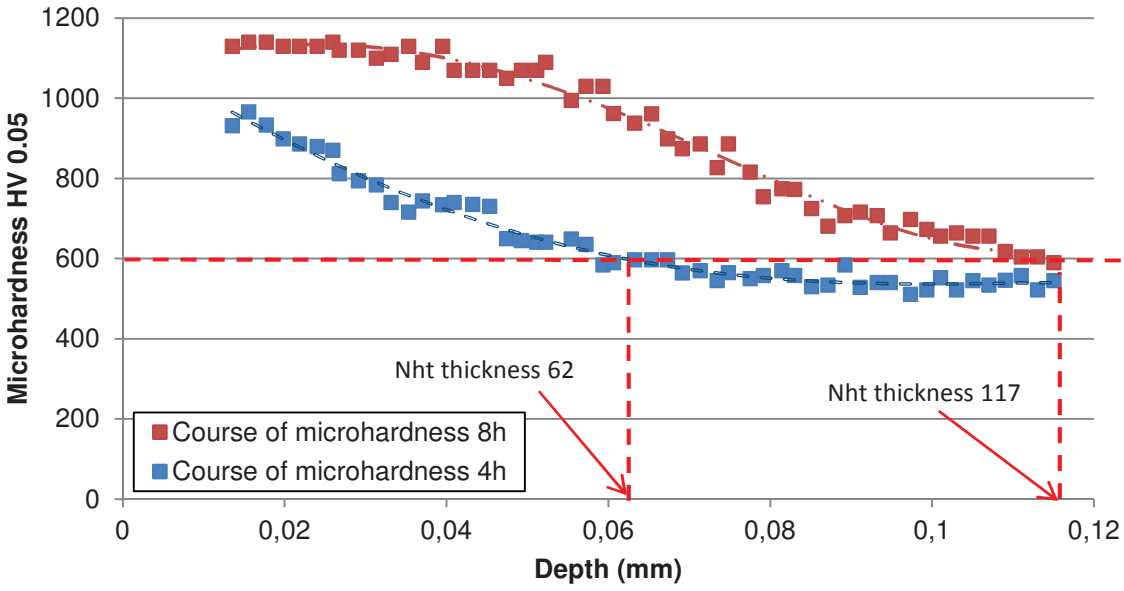

Figure 5 Microharness courses after plasma nitriding 4 and 8 h

4. CONCLUSION

Experimentally it was proven that 1.7765 steel after plasma nitriding process does not occur the redistribution of substitution elements Cr, Mo, Mn (see **Table 4**). The measurement of interstitial elements concentration on the surface and in depth of 12-102 microns is shown in **Figure 4**. In the graphic expression the mutual influence of carbon and nitrogen is noticeable. The concentration of nitrogen is going down by increasing of depth what is shown in **Figure 4**. The carbon concentration is gradually optimized by increasing depth from surface. The dependence of concentration elements carbon - nitrogen and microhardness course has important influence to the mechanical properties of nitrided layer. This phenomenon is given in **Figure 4**. The redistribution of nitrogen in depth of layer shows the influence of process duration on redistribution of nitrogen. Plasma nitriding of 1.7765 after 4 h caused decreasing of surface hardness about 200 HV 0.05 against 8 h process. Nht thickness was increased from 60 to 117 µm.

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